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TITLE: BURN RATE ENHANCEMENT VIA METAL AMINOTETRAZOLE HYDROXIDES

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BURN RATE ENHANCEMENT VIA METAL AMINOTETRAZOLE HYDROXIDES

BACKGROUND OF THE INVENTION

This invention relates generally to gas generant materials such as used in the inflation of automotive inflatable restraint airbag cushions and, more particularly, to the enhancement of the rate at which such materials burn or otherwise react.

Gas generating materials are useful in a variety of different contexts. One significant use for such compositions is in the operation of automotive inflatable restraint airbag cushions. It is well known to protect a vehicle occupant using a cushion or bag, e.g., an "airbag cushion," that is inflated or expanded with gas when the vehicle encounters sudden deceleration, such as in the event of a collision. In such systems, the airbag cushion is normally housed in an uninflated and folded condition to minimize space requirements. Such systems typically also include one or more crash sensors mounted on or to the frame or body of the vehicle to detect sudden decelerations of the vehicle and to electronically trigger activation of the system. Upon actuation of the system, the cushion begins to be inflated in a matter of no more than a few milliseconds with gas produced or supplied by a device commonly referred to as an "inflator." In practice, such an airbag cushion is desirably deployed into a location within the vehicle between the occupant and certain parts of the vehicle interior, such as a door, steering wheel, instrument panel or the like, to

prevent or avoid the occupant from forcibly striking such part(s) of the vehicle interior.

Gas generant compositions commonly utilized in the inflation of automotive inflatable restraint airbag cushions have previously most typically employed or been based on sodium azide. Such sodium azide-based compositions, upon initiation, normally produce or form nitrogen gas. While the use of sodium azide and certain other azide-based gas generant materials was in accordance with industry specifications, guidelines and standards, such use could potentially involve or raise concerns such as relating to the safe and effective handling, supply and disposal of such gas generant materials.

In view thereof, significant efforts have been directed to minimizing or avoiding the use of sodium azide in automotive airbag inflators. Through such efforts, various combinations of non-azide fuels and oxidizers have been proposed for use in gas generant compositions. These non-azide fuels are generally desirably less toxic to make and use, as compared to sodium azide, and may therefore be easier to dispose of and thus, at least in part, found more acceptable by the general public. Further, non-azide fuels composed of carbon, hydrogen, nitrogen and oxygen atoms typically yield all gaseous products upon combustion. As will be appreciated by those skilled in the art, fuels with high nitrogen and hydrogen contents and a low carbon content are generally attractive for use in such inflatable restraint applications due to

their relatively high gas outputs (such as measured in terms of moles of gas produced per 100 grams of gas generant material).

Most oxidizers known in the art and commonly employed in such gas generant compositions are metal salts of oxygen-bearing anions (such as nitrates, chlorates and perchlorates, for example) or metal oxides. Unfortunately, upon combustion, the metallic components of such oxidizers typically end up as a solid and thus reduce the relative gas yield realizable therefrom. Consequently, the amount of such oxidizers in a particular formulation typically affects the gas output or yield from the formulation. If oxygen is incorporated into the fuel material, however, less of such an oxidizer may be required and the gas output of the formulation can be increased.

In addition to low toxicity and high gas outputs, gas generant materials desirably are relatively inexpensive, thermally stable (i.e., desirably decompose only at temperatures greater than about 160°C), and have a low affinity for moisture.

In addition to the above-identified desirable properties and characteristics, gas generant materials for use in automotive inflatable restraint applications must be sufficiently reactive such that upon the proper initiation of the reaction thereof, the resulting gas producing or generating reaction occurs sufficiently rapidly such that a corresponding inflatable airbag cushion is properly inflated so as to provide desired impact protection to an associated vehicle occupant. In general,

the burn rate for a gas generant composition can be represented by the equation (1), below:

$$r_b = k(P)^n \qquad (1)$$

where,

r_b	=	burn rate (linear)
k	=	constant
P	=	pressure
n	=	pressure exponent, where the pressure exponent is the slope of a linear regression line drawn through a log-log plot of burn rate versus pressure.

Guanidine nitrate ($CH_6N_4O_3$) is a non-azide fuel with many of the above-identified desirable fuel properties and which has been widely utilized in the automotive airbag industry. For example, guanidine nitrate is commercially available, relatively low cost, non-toxic, provides excellent gas output due to a high content of nitrogen, hydrogen and oxygen and a low carbon content and has sufficient thermal stability to permit spray dry processing.

Unfortunately, guanidine nitrate suffers from a lower than may be desired burn rate. Thus, there remains a need and a demand for an azide-free gas generant material which may more effectively overcome one or more of the problems or shortcomings described above.

Commonly assigned Mendenhall, U.S. Patent 6,550,808, issued 22 April 2003, relates generally to gas generant compositions which desirably include or contain guanylurea nitrate (also known as dicyandiamidine and amidinourea). In

particular, guanylurea nitrate advantageously has a relatively high theoretical density such as to permit a relatively high loading density for a gas generant material which contains such a fuel component. Further, guanylurea nitrate exhibits excellent thermal stability, as evidenced by guanylurea nitrate having a thermal decomposition temperature of 216°C. In addition, guanylurea nitrate has a large negative heat of formation (i.e., -880 cal/gram) such as results in a cooler burning gas generant composition, as compared to an otherwise similar gas generant containing guanidine nitrate.

While the inclusion or use of guanylurea nitrate in gas generant materials can serve to avoid reliance on the inclusion or use of sodium azide or other similar azide materials while providing improved burn rates and overcoming one or more of the problems, shortcomings or limitations such as relating to cost, commercial availability, low toxicity, thermally stability and low affinity for moisture, even further improvement in the burn rate of gas generant formulations may be desired or required for particular applications.

For some inflator applications, a low gas generant formulation burn rate can be at least partially compensated for by reducing the size of the shape or form of the gas generant material such as to provide the gas generant material in a shape or form having a relatively larger reactive surface area. In practice, however, there are practical limits to the minimum size of the shape or form, such as a tablet, for example, to which gas generant materials can reproducibly be manufactured and

increased burn rates may be needed for particular applications which require a higher inflator performance.

Thus, there is a need and a demand for methods or techniques for increasing the burn rate of a gas generant formulation as well as for non-azide based gas generant formulations having desirably increased or elevated burn rates.

SUMMARY OF THE INVENTION

A general object of the invention is to provide a method for increasing the burn rate of a gas generant formulation as well as an improved gas generant formulation.

A more specific objective of the invention is to overcome one or more of the problems described above.

The general object of the invention can be attained, at least in part, through a method which involves adding a quantity of at least one metal aminotetrazole hydroxide to the gas generant formulation. In accordance with certain preferred embodiments, such metal aminotetrazole hydroxide is copper aminotetrazole hydroxide, zinc aminotetrazole hydroxide and combinations thereof. In specific preferred embodiments, such metal aminotetrazole hydroxide is present in the gas generant formulation in a relative amount of at least about 1 wt.%, at least about 5 wt.% and at least about 10 wt.%, respectively. In certain preferred embodiments, such specified metal aminotetrazole hydroxide is present in the gas generant formulation in a relative amount of at least about 10 wt.% and no more than about 25 wt.%.

The prior art generally fails to provide as effective as may be desired methods or techniques for the raising of the burn rate of a gas generant formulation, particularly a non-azide gas generant formulation, to a level sufficient and desired for vehicular inflatable restraint system applications and in a manner practical and appropriate for such applications. Further, the prior art also generally fails to provide corresponding or associated non-azide gas generant formulations which exhibit sufficiently and effectively elevated burn rates as may be desired for such vehicular inflatable restraint system applications.

In accordance with one preferred embodiment of the invention there is comprehended a method for increasing the burn rate of a gas generant formulation and which method involves including, in the gas generant formulation, a quantity of at least about 1 composition weight percent of copper aminotetrazole hydroxide having an empirical formula of $Cu(CH_2N_5)OH$.

The invention still further comprehends, in accordance with another preferred embodiment of the invention, a gas generant formulation which includes:

a primary fuel component selected from the group consisting of copper bis-guanyl urea dinitrate, guanidine nitrate and mixtures thereof;

a primary oxidizer component selected from the group consisting of ammonium nitrate, basic copper nitrate, copper diammine dinitrate and mixtures of ammonium nitrate and copper diammine dinitrate; and

at least one metal aminotetrazole hydroxide effective to enhance the burn rate of the gas generant formulation as compared to the same gas generant formulation without inclusion of the at least one metal aminotetrazole hydroxide.

As used herein, references to a specific composition, component or material as a "fuel" are to be understood to refer to a chemical which generally lacks sufficient oxygen to burn completely to CO_2, H_2O and N_2.

Correspondingly, references herein to a specific composition, component or material as an "oxidizer" are to be understood to refer to a chemical generally having more than sufficient oxygen to burn completely to CO_2, H_2O and N_2.

Guanylurea nitrate ($NH_2C(NH)NHC(O)NH_2 \circ HNO_3$) is also commonly known as dicyandiamidine and amidinourea.

Other objects and advantages will be apparent to those skilled in the art from the following detailed description taken in conjunction with the appended claims and drawing.

BRIEF DESCRIPTION OF THE DRAWING

The Figure is a simplified schematic, partially broken away, view illustrating the deployment of an airbag cushion from an airbag module assembly within a vehicle interior, in accordance with one embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a method for increasing the burn rate of a gas generant formulation as well as an improved gas generant formulation.

As described in greater detail below and in accordance with one preferred embodiment of the invention, such method desirably involves the addition of a quantity of at least one additive, e.g., a metal aminotetrazole hydroxide such as, preferably, copper aminotetrazole hydroxide, zinc aminotetrazole hydroxide or a combination thereof, to the gas generant formulation. A particularly preferred such additive for use in the practice of the invention is copper aminotetrazole hydroxide, having an empirical formula of $Cu(CH_2N_5)OH$.

Those skilled in the art and guided by the teachings herein provided will appreciate that the invention can desirably be practice via the inclusion of a sufficient quantity of the metal aminotetrazole hydroxide, e.g., copper aminotetrazole hydroxide, zinc aminotetrazole hydroxide or a combination thereof, to the gas generant formulation to effect a desirable increase in the burn rate exhibited by the resulting formulation, as compared to the same formulation without the inclusion of such metal aminotetrazole hydroxide. In general, however, it has been found preferable for a gas generant formulation in accordance with a preferred practice of the invention to include or incorporate such metal aminotetrazole hydroxide additive in a relative amount of at least about 1 wt.%, and, more typically, in a relative amount of at least about 5 wt.%. In accordance with certain preferred embodiments such metal aminotetrazole hydroxide additive is preferably present in a relative amount of at least 10 wt.% in order to provide gas generant formulations evidencing a sufficiently increased burn rate effective for such inflatable restraint system applications. In

accordance with certain preferred embodiments of the invention, such metal aminotetrazole hydroxide additive is preferably present in the gas generant formulation in a relative amount of at least about 10 wt.% and no more than about 25 wt.%.

While the broader practice of the invention is not necessarily limited to the incorporation or use of such a metal aminotetrazole hydroxide in combination or conjunction with particular or specific gas generant formulations, the invention is believed to have particular benefit or utility in gas generant formulations that contain or include either or both guanidine nitrate and copper bis-guanyl urea dinitrate as a primary fuel and a primary oxidizer selected from the group consisting of ammonium nitrate, basic copper nitrate, copper diammine dinitrate and mixtures of ammonium nitrate and copper diammine dinitrate. For example, one preferred gas generant formulation for the incorporation or use of such a metal aminotetrazole hydroxide in accordance with the invention includes ammonium nitrate as a primary oxidizer and copper bis-guanyl urea dinitrate as a primary fuel. Another preferred gas generant formulation for the incorporation or use of such a metal aminotetrazole hydroxide in accordance with the invention includes basic copper nitrate as a primary oxidizer and guanidine nitrate as a primary fuel.

Those skilled in the art and guided by the teachings will further appreciate that various procedures or reaction schemes can be employed in the preparation of a metal aminotetrazole hydroxide in accordance with the invention.

For example, in accordance with one preferred practice of such reaction scheme, a spray-dry mix tank is charged with water. A selected quantity of 5-aminotetrazole is added to the spray-dry mix tank and partially dissolved in or with the water. Cupric hydroxide is then added to the contents of the spray-dry mix tank and the temperature of the slurry equilibrated at 190°F and held at that temperature until the reaction is complete (approximately 1 hour). Other desired gas generant ingredients (e.g., fuel, oxidizer, slagging aids, etc.) are then added to the reaction mixture slurry. The reaction mixture slurry can then be pumped to a nozzle and spray dried. Further processing steps such as blending, pressing, igniter coating, etc. or the like can then be performed per standard procedures.

TABLE 1, below, lists certain select properties of copper aminotetrazole hydroxide in accordance with the invention.

TABLE 1	
PROPERTY	VALUE
Thermal onset of decomposition	150°C
Color	blue/purple powder
Water solubility	sparingly
Content	(mass percent)
- copper	36.72
- carbon	7.44
- hydrogen	2.09
- nitrogen	40.83

As further detailed herein, particular reaction schemes which can be used in the preparation of copper having an empirical formula of $Cu(CH_2N_5)OH$, described above, are shown in reactions 2-4, below:

$$Cu(OH)_2 + CH_3N_5 \text{ (5-aminotetrazole)} \Rightarrow Cu(CH_2N_5)OH + H_2O \qquad (2)$$

$$Cu(NO_3)_2 \cdot 3H_2O + CH_3N_5 + 2NH_4OH \text{ (slight excess)} \Rightarrow Cu(CH_2N_5)OH + 2NH_4NO_3 + 4H_2O + NH_3 \qquad (3)$$

$$Cu(NO_3)_2 \cdot 3H_2O + CH_5N_3CH_3N_5 \text{ (guanidinium aminotetrazole)} + NH_4OH \text{ (slight excess)} \Rightarrow Cu(CH_2N_5)OH + CH_5N_3HNO_3 + NH_4NO_3 + 3H_2O + NH_3 \qquad (4)$$

As detailed below, the reaction scheme shown in reaction (2) has been currently found to be preferred.

As will be appreciated, gas generant compositions or materials prepared in accordance with the invention can be incorporated, utilized or practiced in conjunction with a variety of different structures, assemblies and systems. As representative, the Figure illustrates a vehicle 10 having an interior 12 wherein is positioned an inflatable vehicle occupant safety restraint system, generally designated by the reference numeral 14. As will be appreciated, certain standard elements not necessary for an understanding of the invention may have been omitted or removed from the Figure for purposes of facilitating illustration and comprehension.

The vehicle occupant safety restraint system 14 includes an open-mouthed reaction canister 16 which forms a housing for an inflatable vehicle occupant restraint 20, e.g., an inflatable airbag cushion, and an apparatus, generally designated by the reference numeral 22, for generating or supplying inflation gas for the inflation of an associated occupant restraint. As identified above, such a gas generating device is commonly referred to as an "inflator."

The inflator 22 contains a quantity of a gas generant composition or formulation in accordance with the invention and such as suited, upon ignition, to produce or form a quantity of gas such as to be used in the inflation the inflatable vehicle occupant restraint 20. As will be appreciated, the specific construction of the inflator device does not form a limitation on the broader practice of the invention and such inflator devices can be variously constructed such as is also known in the art.

In practice, the airbag cushion 20 upon deployment desirably provides for the protection of a vehicle occupant 24 by restraining movement of the occupant in a direction toward the front of the vehicle, i.e., in the direction toward the right as viewed in the Figure.

The present invention is described in further detail in connection with the following examples which illustrate or simulate various aspects involved in the practice of the invention. It is to be understood that all changes that come within the spirit of the invention are desired to be protected and thus the invention is not to be construed as limited by these examples.

EXAMPLES

Example 1 - Preparation of copper aminotetrazole hydroxide via reaction (2), above.

In this Example, 4.66 grams of 5-aminotetrazole was dissolved in 25 ml of water. Basic copper nitrate, in an amount of 5.34 grams, was added to this mixture. The resulting slurry was stirred and heated to 80°C. The heated slurry was held at this temperature for approximately one half hour, until the color of the slurry changed from green to purple.

Example 2 - Preparation of copper aminotetrazole hydroxide via reaction (3), above.

In this Example, 6.09 grams of cupric nitrate trihydrate was dissolved in 25 ml of water. To this mixture was added 5-aminotetrazole in an amount of 2.14 grams. The resulting solution was stirred and heated to 80°C. Approximately 2.87 grams of a 30% ammonium hydroxide solution was then added to this heated solution. Since, after several minutes of stirring, the resulting slurry was still green in color, a 30% ammonium hydroxide solution was added dropwise to the slurry until the slurry changed in color, from green to purple.

Example 3 - Preparation of copper aminotetrazole hydroxide via reaction (4), above.

In this Example, 5.74 grams of cupric nitrate trihydrate was dissolved in 25 ml of water. Guanidinium aminotetrazole, in an amount of 3.42 grams, was added to this mixture. The resulting solution was stirred and heated to 80°C.

Approximately 1.35 grams of a 30% ammonium hydroxide solution was then added to this heated solution. Since, after several minutes of stirring, the resulting slurry was still green in color, a 30% ammonium hydroxide solution was added dropwise to the slurry until the slurry changed in color, from green to purple.

Examples 4 and Comparative Example 1.

In these tests, 100 grams of each of the gas generant formulations having the compositions identified in TABLE 2 below were prepared using the following procedure:

The guanidine nitrate (GN) and 5-aminotetrazole were predissolved in water. Cupric hydroxide was added and allowed to react, as in Example 1, described above. After the reaction was completed, a dry blend of the remaining formulation solids (e.g., basic copper nitrate and Al_2O_3) were stirred in, mixed well and the resulting composition vacuum oven dried at 80°C.

TABLE 2

	EXAMPLE 4	COMPARATIVE EXAMPLE 1
BCN	45.26	45.97
GN	33.22	52.53
$Cu(CH_2N_5)OH$	20.02	- 0 -
Al_2O_3	1.50	1.50

where,

BCN = basic copper nitrate and
GN = guanidine nitrate.

The gas generant formulation of each of Example 4 and Comparative Example 1 was then tested. The burn rate and density (ρ) values identified in TABLE 3 below were obtained. In particular, the burn rate data was obtained by first pressing samples of the respective gas generant formulations into the shape or form of a 0.5 inch diameter cylinder using a hydraulic press (12,000 lbs force). Typically enough powder was used to result in a cylinder length of 0.5 inch. The cylinders were then each coated on all surfaces except the top one with a krylon ignition inhibitor to help ensure a linear burn in the test fixture. In each case, the so coated cylinder was placed in a 1-liter closed test vessel capable of being pressurized to several thousand psi with nitrogen and equipped with a pressure transducer for accurate measurement of the pressure within the test vessel. A small sample of igniter powder was placed on top of the cylinder and a nichrome wire was passed through the igniter powder and connected to electrodes mounted in the test vessel lid. The test vessel was then pressurized to the desired pressure and the sample ignited by passing a current through the nichrome wire. Pressure vs. time data was collected as each of the respective samples were burned. Since combustion of each of the samples generated gas, an increase in test vessel pressure signaled the start of combustion and a "leveling off" of pressure signaled the end of combustion. The time required for combustion

was equal to $t_2 - t_1$ where t_2 is the time at the end of combustion and t_1 is the time at the start of combustion. The sample weight was divided by combustion time to give a burning rate in grams per second. Burning rates were typically measured at four pressures (900, 1350, 2000, and 3000 psi). The log of burn rate vs the log of average pressure was then plotted. From this line the burn rate at any pressure can be calculated using the gas generant composition burn rate equation (1), identified above. The results are shown in TABLE 3, below.

TABLE 3		
	EXAMPLE 4	COMPARATIVE EXAMPLE 1
r_b	0.66	0.52
n	0.43	0.54
k	0.035	0.013
ρ (g/cc)	2.05	1.91

where,

r_b = burn rate at 1000 psi in inch per second (ips);

n = pressure exponent in the burn rate equation (1) identified above, where the pressure exponent is the slope of the plot of the log of pressure along the x-axis versus the log of the burn rate along the y-axis; and

k = the constant in the burn rate equation (1) identified above.

Discussion of Results

As shown in TABLE 3, the gas generant formulation of Example 4, which gas generant formulation contained copper aminotetrazole hydroxide, in

accordance with a preferred practice of the invention, experienced a significantly increased burn rate (r_b) as compared to the gas generant formulation of Comparative Example 1.

Further, as the pressure exponent (n) generally corresponds to the performance sensitivity of the respective gas generant material, with a lower burn rate pressure exponent corresponding to a gas generant material which desirably exhibits corresponding lesser or reduced pressure sensitivity, these examples show that the inclusion of the copper aminotetrazole hydroxide, in accordance with a preferred practice of the invention, can desirably increase the burn rate of the gas generant formulation without significantly increasing the pressure sensitivity of the resulting formulation.

As also shown in TABLE 4, the gas generant formulation of Example 4 and in accordance with the invention had a density which was significantly greater than the gas generant formulation of Comparative Example 1. Those skilled in the art and guided by the teachings herein provided will appreciate that gas generant formulations of increased density can desirably be used such as to increase the volume of gas produced on a unit volume basis and thereby at least partially offset any decrease in the moles of gas produced on a mass basis associated with replacement of some of the guanidine nitrate with the copper aminotetrazole hydroxide, in accordance with the invention.

Example 5 and Comparative Example 2.

In these tests, 100 gram batches of the gas generant formulations identified in TABLE 4 below were prepared. Note the formulations were otherwise similar except for the inclusion of copper aminotetrazole hydroxide in Example 5. The formulations each contained ammonium nitrate as the primary oxidizer, copper bis-guanyl urea dinitrate as the primary fuel, and silicon dioxide also as an additive, e.g., a slagging agent.

TABLE 4		
	EXAMPLE 5	COMPARATIVE EXAMPLE 2
Ammonium nitrate	53.04	53.16
Copper bis-guanyl urea dinitrate	23.45	43.36
Silicon dioxide	3.49	3.50
Copper aminotetrazole hydroxide	20.02	-0-

The gas generant formulation of each of Example 5 and Comparative Example 2 was then tested. The burn rate and density (ρ) values identified in TABLE 5 below were obtained. The burn rate data was obtained in the same general manner described above relative to Example 4 and Comparative Example 1 with the samples being pressed into a cylinder shape or form, coated, placed in a closed test vessel with a small sample of igniter powder placed on top of the cylinder and a nichrome wire was passed through the igniter powder and connected to electrodes

mounted in the test vessel lid. The test vessel was then pressurized to the desired pressure and the sample ignited by passing a current through the nichrome wire. Pressure vs. time data was collected as each of the respective samples were burned. Since combustion of each of the samples generated gas, an increase in pressure within the test vessel signaled the start of combustion and a "leveling off" of pressure signaled the end of combustion. The time required for combustion was equal to $t_2 - t_1$ where t_2 is the time at the end of combustion and t_1 is the time at the start of combustion. The sample weight was divided by combustion time to give a burning rate in grams per second. Burning rates were typically measured at four pressures (900, 1350, 2000, and 3000 psi). The log of burn rate vs the log of average pressure was then plotted. From this line the burn rate at any pressure can be calculated using the gas generant composition burn rate equation (1), identified above.

TABLE 5

	EXAMPLE 5	COMPARATIVE EXAMPLE 2
r_b	0.52	0.30
n	0.58	0.66
k	0.009	0.003
ρ (g/cc)	1.88	1.82

where,

r_b = burn rate at 1000 psi in inch per second (ips);

n = pressure exponent in the burn rate equation (1) identified above, where the pressure exponent is the slope of the plot of the log of pressure along the x-axis versus the log of the burn rate along the y-axis; and

k = the constant in the burn rate equation (1) identified above.

Discussion of Results

As shown in TABLE 5, the gas generant formulation of Example 5, which gas generant formulation contained copper aminotetrazole hydroxide, in accordance with a preferred practice of the invention, experienced a significantly increased burn rate (r_b) as compared to the gas generant formulation of Comparative Example 2.

Further, the gas generant formulation of Example 5 exhibited a lesser or reduced pressure sensitivity as compared to the gas generant formulation of Comparative Example 2, as evidenced by the lower or decreased pressure exponent (n) obtained therewith.

Thus, the invention provides an effective method or technique for desirably raising or increasing of the burn rate of a gas generant formulation, particularly a non-azide gas generant formulation, to a level sufficient and desired for vehicular inflatable restraint system applications and in a manner practical and appropriate for such applications. Further, the invention also provides corresponding or associated non-azide gas generant formulations which exhibit sufficiently and

effectively elevated burn rates as may be desired for such vehicular inflatable restraint system applications.

The invention illustratively disclosed herein suitably may be practiced in the absence of any element, part, step, component, or ingredient which is not specifically disclosed herein.

While in the foregoing detailed description this invention has been described in relation to certain preferred embodiments thereof, and many details have been set forth for purposes of illustration, it will be apparent to those skilled in the art that the invention is susceptible to additional embodiments and that certain of the details described herein can be varied considerably without departing from the basic principles of the invention.